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CERAMIC MATERIALS BASED ON DIOPSIDE

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The effect of diopside raw material with a high diopside content on the properties of construction ceramics from pastes containing diopside concentrate (85, 90, and 95%) with dispersion of up to 150 μm and sodium silicate glass was investigated. The possibility of using natural diopside, obtained in primary processing of concentrate without wet milling of the batch, in ceramic pastes as the basic component was demonstrated.

Key words: diopside concentrate, sodium silicate glass, ceramic paste, shrinkage, water absorption, strength.

The development of industrial and civil construction has made it necessary to increase production and use of environmentally clean, competitive, and at the same time, inexpensive wall and facing ceramic articles.

The observed increase in the production volumes of ceramic construction materials confirms the prospects for development of the ceramics industry and expansion of the assortment and competitiveness of ceramic construction materials in the internal market make their use promising.

We used natural diopside with dispersion under 150 μm in manufacture of facing construction materials.

Sufficient experience in use of diopside ($CaMgSi_2O_6$) in ceramics production has now accumulated [1, 2]. Diopside rocks from the southern Baikal region are distinguished by a high degree of purity with respect to iron oxides and other coloring oxides [3].

Diopside rocks have been investigated both in production of high-frequency ceramics [4] and in fine construction ceramics [2] and porcelain pastes [4, 5]. Processing of diopside from the mica group of deposits, namely, the Burutuisky deposit, have now begun to be developed.

The studies by colleagues in the Department of Silicate and Nanomaterials Technology at Tomsk Polytechnical University on the use of diopside raw material in ceramic pastes show that diopside-containing raw material ensures sintering of different ceramic pastes due to reaction with clay components in the solid phase until a melt appears. Their use allows changing the importance of clay in ceramic pastes, retaining the role of binder that ensures the strength of molded articles. Diopside rocks with an approximately 50%[4] diopside content are suitable for increasing the quality of facing tiles. The presence of up to 30% quartz and calcite in diopside rock does not reduce the quality. With an increase in the amount of diopside in the rock, the quality of the tiles increases. We attempted to obtain ceramic material made of compositions of diopside concentrate (up to 150 μm) with liquid glass.

Diopside concentrate and sodium silicate glass were investigated as components of the ceramic paste. The amount of diopside concentrate in the ceramic paste varied from 85 to 95%.

In the diopside rocks in the Burutuiskoe deposit, the iron oxide content varies from 2.0% in the surface layer to thousandths of a percent in the basic mass (Table 1). The diopside content increases over the depth, gradually increasing to 80%. Quartz acts as the basic extrinsic mineral in the rock. In the upper layer, the quartz content reaches 50%. The diopside concentrate is obtained from the middle layer, where the Fe_2O_3 content is 0.65%.

Sodium silicates in the form of liquid glass were used as the component that activates sintering and acts as a process binder in molding.

The chemical composition of each component was quantitatively calculated by x-ray spectral fluorescence analysis on a SRS-303 instrument. The chemical composition is reported in Table 2, and the component composition of the ceramic pastes is given in Table 3.

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[4] Here and below, mass content.

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TABLE 1. Chemical Composition of Diopside Rocks from Different Depths in the Burutuiskoe Deposit

Diopside rock	Mass content of oxides, %								
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O
Upper layer (capping)	56.50	0.07	0.99	1.18	25.94	13.61	0.03	0.9	0.17
Middle layer (intermediate)	57.11	0.31	2.23	0.65	23.57	14.27	0.05	0.15	0.21
Lower layer (basic rock mass)	54.29	–	0.22	0.03	26.39	14.35	0.01	0.10	0.15

TABLE 2. Chemical Composition of Components

Component	Mass fraction, %							
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Diopside concentrate	54.41	0.01	1.2	0.65	26.21	17.31	0.17	0.04
Soluble sodium silicate glass	74.70	–	–	–	–	–	25.3	–

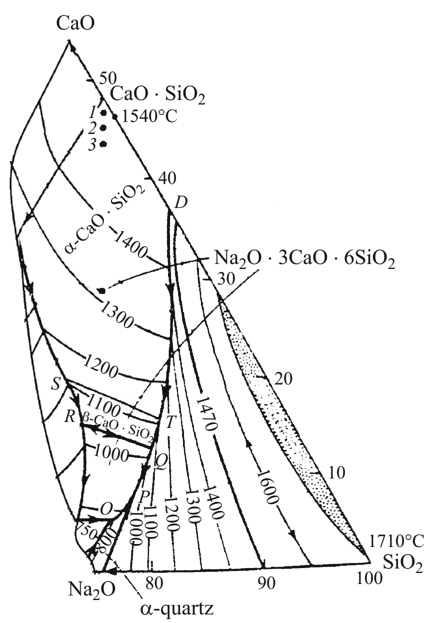

Fig. 1. Region of the diagram of the Na_2O – CaO – SiO_2 system.

The boundaries of the temperature regime for sintering the ceramic pastes (points *1*, *2*, and *3* in Fig. 1) were determined based on an analysis of the Na_2O – CaO – SiO_2 phase diagram, where MgO was converted to CaO.

TABLE 3. Component Composition of Ceramic Pastes

Component	Mass content of component, %, in compositions		
	1	2	3
Diopside concentrate	95	90	85
Soluble sodium silicate glass	5	10	15

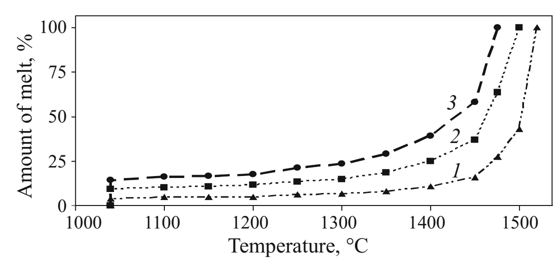

Fig. 2. Fusibility curves of ceramic pastes: *1*) 95% diopside, 5% sodium silicate glass; *2*) 90% diopside, 10% sodium silicate glass; *3*) 85% diopside, 15% sodium silicate glass.

In the Na_2O – CaO – SiO_2 phase diagram, the points of the compositions containing diopside and liquid glass are in the crystallization field of wollastonite.

The fusibility curves were plotted with the Na_2O – CaO – SiO_2 phase diagram (Fig. 2).

The analysis of the fusibility curves of these ceramic pastes in the Na_2O – CaO – SiO_2 system theoretically shows that the compositions are characterized by a small amount of primary melt, from 3.9% (composition *1*) to 14.3% (composition *3*) at the temperature of 1040°C. The amount of primary melt increases with an increase in the percentage content of diopside and a decrease in liquid glass. The amount of melt increases beginning at 1240°C. At 1475°C, 100% melt content is attained. The pastes are characterized by a wide sintering range of the order of 200°C. Since magnesium and about 0.65% iron contaminants are present in the diopside in addition to calcium, the primary melt temperature is proposed below.

In the experiments, firing was conducted from 800 to 1250°C in the sintering interval range.

The x-ray phase analysis showed the presence of primarily diopside in the samples.

The physicomechanical properties of the ceramic pastes were determined on standard cylindrical samples molded

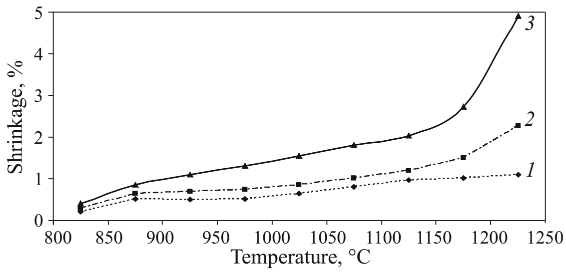

Fig. 3. Change in shrinkage of samples after firing at different temperatures: *1*) 95% diopside, 5% sodium silicate glass; *2*) 90% diopside, 10% sodium silicate glass; *3*) 85% diopside, 15% sodium silicate glass.

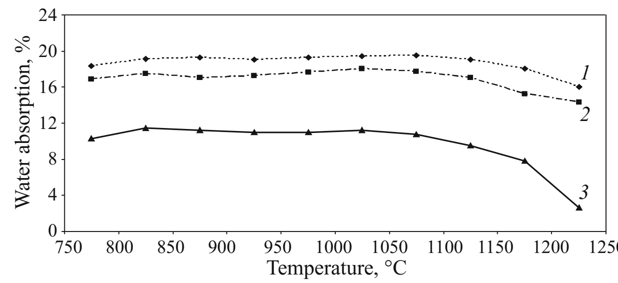

Fig. 4. Change in water absorption of samples after firing at different temperatures: *1*) 95% diopside, 5% sodium silicate glass; *2*) 90% diopside, 10% sodium silicate glass; *3*) 85% diopside, 15% sodium silicate glass.

from wet paste (25%) in a press, dried, and fired at different temperatures — from 800 to 1250°C.

After firing, the shrinkage, water absorption, and compressive strength parameters were determined.

The shrinkage, water absorption, and strength of the fired samples at different temperatures are shown in Figs. 3, 4, and 5.

The curves of the change in the shrinkage (Fig. 3) show that there is a linear increase in the shrinkage up to 1150°C for the sample with a sodium silicate glass content of 5 to 10%. The shrinkage increases slightly to 1.09% from 1200°C for the sample with the lowest sodium silicate glass content (5%) and to 2.27% for the sample containing 10% sodium silicate glass. The sample containing a smaller amount of diopside (85%) and larger amount of sodium silicate glass (15%) underwent the greatest shrinkage, and it increased to 1.3% after 1000°C and 4.9% at 1250°C.

The analysis of the change in the water absorption of the samples (Fig. 4) as a function of the firing temperature shows that the water absorption also changes similar to the shrinkage. The water absorption of the samples with a 90 – 95% diopside and a 5 – 10% liquid glass content was approximately the same over the entire firing time and was from 18.4 to 14%. When the diopside in the ceramic pastes was decreased to 85% and the liquid glass was increased to 15%, the water absorption parameter was much lower and was 10.32% at 800°C, gradually decreased after 1100°C, and attained 2.64% at 1250°C.

The strength of the samples as a function of the firing temperature reflects the change in the shrinkage and water absorption. The analysis of the change in the compressive

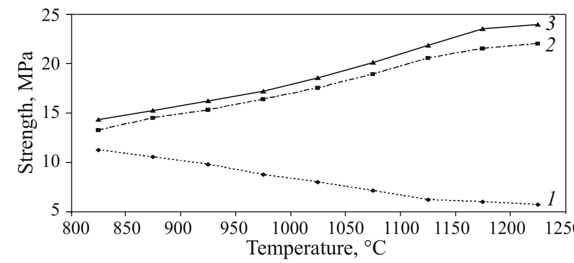

Fig. 5. Change in strength of samples after firing at different temperatures: *1*) 95% diopside, 5% sodium silicate glass; *2*) 90% diopside, 10% sodium silicate glass; *3*) 85% diopside, 15% sodium silicate glass.

strength of the samples showed that they have sufficiently high strength (11 – 14 MPa) after firing at 800°C. The strength of the sample with 95% diopside and 5% liquid glass at the firing temperature of 800°C is much lower than the strength of the samples containing a smaller amount of diopside and more liquid glass, and on subsequent firing it decreased from 11 to 5 MPa, which is in agreement with the change in the shrinkage. We can hypothesize that the sodium silicate glass reacts with the diopside without forming a melt. When a large amount of liquid glass is added to the batch, the strength increases from 13 (composition *2*) to 14 MPa (composition *3*) at 800°C, followed by a smooth increase to 24 MPa for the first composition and to 22 MPa for the second composition at 1250°C.

Based on the analysis of the results of the study, we can conclude that the composition containing 85% diopside and

TABLE 4. Physicochemical Properties of Ceramics from a Batch Containing 85% Diopside and 15% Sodium Silicate Glass after Firing at Temperatures from 800 to 1250°C

Characteristic	Firing temperature, °C							
	800	900	1000	1050	1100	1150	1200	1250
Shrinkage, %	0.20	0.85	1.30	1.55	1.80	2.03	2.72	4.90
Water absorption, %	10.32	11.26	11.02	11.25	10.80	9.53	7.80	2.64
Strength, MPa	14.15	15.26	17.20	18.56	20.15	21.85	23.52	23.98

15% sodium silicate glass is optimum for production of facing ceramics (Table 4).

The properties of the ceramic samples made from paste containing 85% diopside (150 μm) and 15% sodium silicate in the form of liquid glass satisfy the basic requirements for ceramic facing materials and have the best relationship between the indexes, i.e., the water absorption does not exceed 10%, the shrinkage is minimal and varies within 0.2 – 4.9%, and the strength is high enough, from 14 to 20 MPa, at firing temperatures from 800 to 1100°C.

The possibility of using natural diopside, obtained in primary processing of concentrate without wet grinding of the batch, as the basic component in ceramic pastes was thus established.

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